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Measurement of PCDD/Fs emissions from a coal–fired power plant in Malaysia and establishment of emission factors

Mutahharah M. Mokhtar [1], Rozainee M. Taib [1], Mimi H. Hassim [1,2]

[1] Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[2] Institute of Hydrogen Economy (IHE), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

ABSTRACT

This paper presents the PCDD/Fs emissions measured from a coal–fired power plant in Malaysia. The study discusses partitioning of PCDD/Fs in particle and gas phase, effects of coal quality to PCDD/Fs formation, effects of air pollution control device (APCD) configuration to PCDD/Fs formation and establishment of emission factors of PCDD/Fs from the studied coal–fired power plant. The results presented in this study were mostly in good agreement with the previous works on PCDD/Fs emissions conducted in other countries. Laboratory analysis results showed that PCDFs were the dominant congeners. The emissions of PCDD/Fs were low which most probably due to the high combustion efficiency. The PCDFs/PCDDs ratio was more than 1 and PCDD/Fs were detected in fly ash, hence speculating that the formation of PCDD/Fs during coal combustion was mainly through *de novo* synthesis. Analysis on partitioning of PCDD/Fs showed that the compounds were mainly emitted in gas phase. This study also indicated that type of coal influenced the formation of PCDD/Fs during coal combustion where bituminous coal with high sulfur (S) content resulted in slightly lower PCDD/Fs emissions compared to sub–bituminous coal. It was also found that operation of flue gas desulfurization (FGD) reduced the emission of PCDD/Fs. The established emission factors for PCDD/Fs were in the range of 0.08 to 0.11 ng I–TEQ/kg.

Keywords: PCDD/Fs, coal–fired power plant, combustion, emission, air pollution control, Malaysia

Corresponding Author:
Mimi H. Hassim
☎ : +60-7-5535548
🖷 : +60-7-5588166
✉ : mimi@cheme.utm.my

1. Introduction

Polychlorinated dibenzo–p–dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) or commonly known as dioxins and furans are the pollutants from industrial processes of most concerned. PCDD/Fs are characterized as having low water solubility, low vapor pressure, highly persistent and tend to bioaccumulate. There are 75 PCDDs and 135 PCDFs where the toxicity of each compound is represented by toxic equivalent factor (TEF) developed by various agencies (Table 1). Based on the TEF value developed by the North Atlantic Treaty Organization (NATO), the most toxic congener is 2,3,7,8–tetrachloro–dibenzo–para–dioxin (2,3,7,8–TCDD) with TEF value of 1 (i.e. the TEF of other compounds is less than 1). Meanwhile, World Health Organization (WHO) indicates 2,3,7,8–TCDD and 1,2,3,7,8–PCDD as having similar toxicity level with TEF value of 1.

As described in McKay (2002) and U.S. EPA (2006), the formation of PCDD/Fs can be divided into three mechanisms; feed content, precursor and *de novo* synthesis which are further discussed below:

Mechanism 1: Presence of PCDD/Fs content in fuel. This mechanism involves PCDD/Fs contained in the feed passing through the combustion chamber without being destroyed and subsequently released into the environment. Zhang et al. (2012) in their study, confirmed the presence of PCDD/Fs in municipal solid waste. Even though to the authors' knowledge, there is no reported PCDD/Fs content in coal, the presence of chlorine (Cl) in coal is indicative of dioxin emissions from coal combustion. Thomas and Spiro (1995) have reported that in the absence of effective air pollution control

systems, dioxin emissions increased with Cl content in fuel. Dioxin emission inventory presented by Thomas and Spiro (1995) shows that low emission of PCDD/Fs from coal combustion is consistent with its low Cl content.

Mechanism 2: Precursor formation. This mechanism involves thermal breakdown and molecular rearrangement of aromatic precursors either originating in the feed or forming as a product of incomplete combustion (PIC) e.g. soot. Examples of pre–cursor compounds are chlorobenzenes and chlorophenols (Huang and Buekens, 1995; Altwicker, 1996; McKay, 2002). The PCDD/Fs formation could occur in homogeneous gas–phase or heterogeneous solid–phase chemistry. The former occurs at higher temperature of 500 to 800 °C while the latter at cool down temperature of 200 to 400 °C.

Mechanism 3: *De novo* synthesis. This mechanism occurs as a result of elementary reactions of appropriate elements such as carbon, hydrogen, oxygen and chlorine atoms. It is a heterogeneous solid–phase formation of PCDD/Fs in the post–combustion environment on the surface of fly ash. It involves oxidation of carbon particulate catalyzed by a transition metal in particular $CuCl_2$ (Ryu et al., 2005) in the presence of chlorine to yield precursor compounds. Huang and Buekens (1995) suggested that *de novo* synthesis could be the dominant mechanism of PCDD/Fs formation in combustion processes.

PCDD/Fs could be emitted from primary and secondary sources. Primary sources include industrial and thermal processes such as waste incineration, combustion of fossil fuels, iron and steel industries, road transport, etc. Secondary sources or

reservoirs are those matrices where PCDD/Fs are already present, either in the environment (i.e. landfills, contaminated soil and sediment) or as products (i.e. sewage, liquid manure, sludge) (UNEP, 1999). Dioxin emission inventory compiled by the UNEP (1999) shows that waste incineration is the major source of dioxin emissions, however, this only applies for countries that operate municipal solid waste (MSW) incinerators. In the absence of large MSW incinerators such as in Australia, the major dioxin emitter is uncontrolled combustion, followed by ferrous and non–ferrous metal production, production of chemicals and consumer goods, and power generation (Bawden et al., 2004). This indicates that the quantity of PCDD/Fs emissions depend on the presence and number of emission sources. New Zealand emission inventory (Ministry for the Environment, 2011) shows that fuelling electricity generating units with coal resulted in increasing of PCDD/Fs emissions compared to firing with natural gas. With reduction of PCDD/Fs emissions from modern incinerators (Nzihou et al., 2012), it is anticipated that in the event of increasing coal consumption, coal–fired power plants could be the major source of PCDD/Fs emissions.

Table 1. *Toxic equivalent factors (TEF)*

Compound	I-TEF (NATO)	WHO-TEF (2005)
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.0003
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.03
2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
1,2,3,4,6,7,8,9-OCDF	0.001	0.0003

Industries commonly practice combustion control or installation of control technologies to reduce PCDD/Fs emissions. Among the good plant practices to achieve reduction of PCDD/Fs emissions are fuel specification to prevent the use of contaminated fuels, use of low moisture pulverized fuels and maintaining good combustion conditions such as operating temperature in excess of 900 °C and residence time of at least 2 s (Ministry for the Environment, 2011). A report by Nescaum (2011) shows that control technologies such as activated carbon injection (ACI) could reduce PCDD/Fs emission in a coal–fired power plant while technologies such as selective catalytic reactor, particulate controls and dry sorbent injection have a co–benefit in reducing PCDD/Fs emissions. A study by Chi et al. (2005) demonstrated that ACI and bag filter could effectively remove vapor phase and particle phase PCDD/Fs respectively.

There were several existing studies on PCDD/Fs emissions from coal–fired power plants in countries such as Spain (Fernandez–Martinez et al., 2004), Netherlands (Meij and Winkel, 2007), Taiwan (Lin et al., 2007) and Poland (Grochowalski and Konieczynski, 2008). These studies generally reported PCDD/Fs emission levels and establishment of emission factors with no emphasis on PCDD/Fs emissions from different type of coals and effects of air pollution control measures used in the plants. Some of the findings of these studies are summarized in Section 3.1.

Coal–fired power plants in Malaysia. In Malaysia, fuel diversification strategy has been practiced since year 1980 to achieve balanced utilization of natural gas, coal, oil, hydro and renewable energy. The development of coal–fired power plant started in year 1987 and currently, there are a total of four coal–fired power plants in Peninsular Malaysia and a number in East Malaysia. Tenaga Nasional Berhad (TNB), the largest electric utility provider in Malaysia recorded increasing coal consumption in Peninsular Malaysia reaching up to 16 million ton/year in 2010 and is expected to further increase due to the expansion of the existing coal–fired power plants. Thus, it is imperative to have a study on emissions from coal–fired power plants in Malaysia.

However to date, there has been no study reporting not only on PCDD/Fs emissions but also other pollutant emissions from Malaysian coal–fired power plants. It should be noted that Malaysia Environmental Quality (Dioxins and Furans) Regulations 2004 only applies to incineration process with specified limit of 0.1 ng I–TEQ/Nm^3. This indirectly led to lesser attention given to emissions of the pollutants from other processes. Recently, a Proposed New Environmental Quality (Clean Air) Regulation 201X (Draft) imposes PCDD/Fs limit to other processes including power generation using fossil fuels. In this paper, the measurement of PCDD/Fs emissions from a coal–fired power plant in Malaysia was presented which discussed (1) partitioning of PCDD/Fs in particle and gas phase (2) effects of coal quality to PCDD/Fs formation, (3) effects of air pollution control device (APCD) configuration to PCDD/Fs formation and (4) establishment of emission factors of PCDD/Fs from the studied coal–fired power plant.

2. Materials and Methods

2.1. Plant description

The findings presented in this paper are based on measurements conducted at one coal–fired power plant in Malaysia. The description of the power plant is provided in Table 2.

Table 2. *Basic information of the studied coal–fired power plant*

Plant capacity (MW)	3x700
Total coal consumption (kg/h)	833x10^3
Coal consumption for each unit (kg/h)	2.8x10^5
Air pollution control device (APCD)	Cold-side electrostatic precipitator (ESP) (upstream), Seawater flue gas desulfurization (FGD) (downstream)
Number of stacks	3
Stack height (m)	200
Stack diameter (m)	7.42
Velocity (m/s)	22.6
Flow rate of flue gas (Nm^3/h)	2.15x10^6

2.2. Coal quality and firing method

The studied coal–fired power plant burned sub–bituminous and bituminous coal imported from Indonesia, Australia and South Africa. Generally, sub–bituminous coal is characterized by a lower calorific value (CV), carbon (C) and sulfur (S) content compared to bituminous coal. The plant practices coal blending before firing. The plant receives three types of coal qualities of different S content e.g. high (0.8 wt% S content), medium and low (about 0.1 wt% S). The coals are stockpiled in the coal yard according to the different S content. Prior to feeding into furnace, stacker reclaimer will grab and mix the coals before dumping the mixture into conveyor to the feeder of the furnace. For the purpose of this study, emissions of PCDD/Fs were measured from separate combustion of two types of coal as described in Table 3.

Prior to entering the furnace, the coal is pulverized to size of 200 Mesh to increase the surface area and further enhance combustion process. The coal is burned at temperature >1 000 °C. The flue gas temperature downstream combustion chamber is in the range of 340 to 380 °C. The temperature before entering ESP is around 150 °C. The flue gas temperature is further decreased to 100 °C at FGD, whereas when FGD is off, the temperature is around 150 °C.

2.3. Sampling method

Sampling of PCDD/Fs at the studied coal–fired power plant was conducted in accordance with U.S. EPA Method 23a (U.S. EPA, 1996). The sampling train (Apex Instruments Model MC–500 Series Isokinetic Source Sampler) is depicted in Figure 1. Flue gas was sampled from the stack isokinetically at each pre–determined traverse point (at isokinetic rate of 90 to 110%) and was led

through a 90 mm micro glass fiber filter (Advantec) in which the dust particles were retained. The flue gas was then cooled to less than 20 °C by passing through a water–cooled condenser. The flue gas was then led to a packed column of adsorbent material of XAD–2 resin. PCDD/Fs in particle phase were collected by filter while the compounds in gas phase were collected by XAD–2 resin.

Stack measurements were conducted for four runs during combustion of sub–bituminous and bituminous coal with and without FGD in operation. The stack sampling configurations were designed as shown in Table 4 in order to study the partitioning of PCDD/Fs in particulate and gas phase as well as the effects of coal type and operation of FGD to emissions of PCDD/Fs from the studied coal–fired power plant. It should be noted that ESP was in operation for all runs. For run 4, the produced fly ash was collected for PCDD/Fs analysis.

Table 3. *Characteristics of sub-bituminous and bituminous coal used in the studied coal–fired power plant*

Analysis	Sub-bituminous	Bituminous
General		
Gross CV (kcal/kg)	4 970	6 060
Total moisture (%) arb [a]	25.1	9.00
Total sulfur (%) arb [a]	0.09	0.75
Proximate analysis		
Ash (%) arb [a]	2.07	12.3
Volatile matter (%) arb [a]	37.92	26.7
Fixed carbon (%) arb [a]	34.91	51.7
Ultimate analysis		
Carbon (C) (%)	68.4	71.54
Hydrogen (H) (%)	3.85	4.33
Oxygen (O) (%)	24.05	7.63
Nitrogen (N) (%)	0.82	1.80
Sulfur (S) (%)	0.12	0.82

[a] *As received basis*
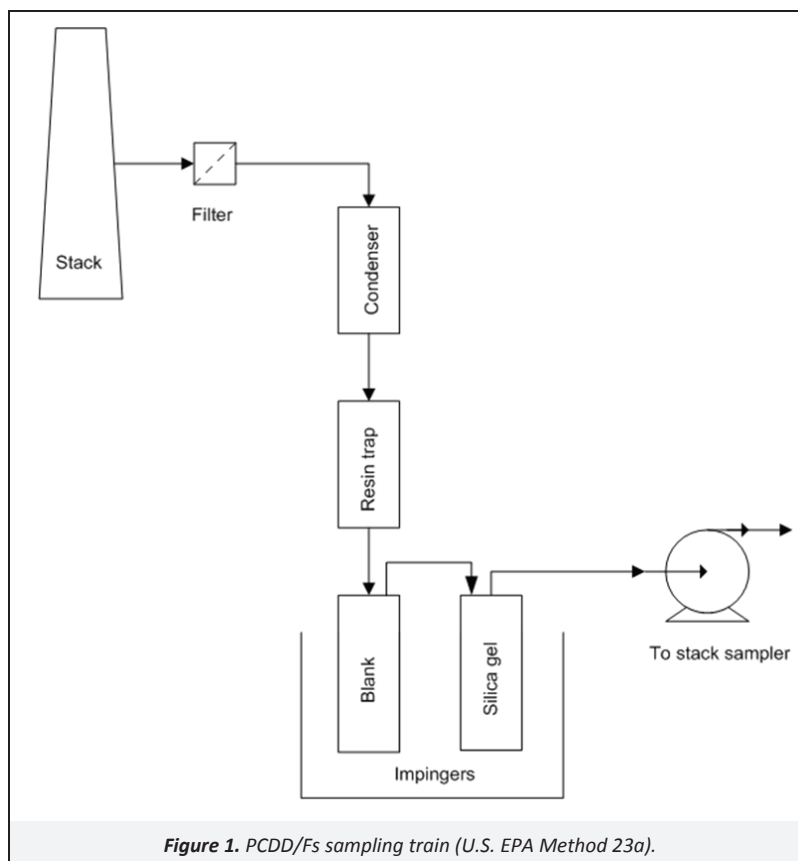

Figure 1. *PCDD/Fs sampling train (U.S. EPA Method 23a).*

Table 4. *Stack sampling configurations and the analyzed sampling media*

Run ID	Coal Type	FGD Operation	Analyzed Sampling Media
1	Sub–bituminous	Off	R [a]+F [b]
2	Sub–bituminous	On	R+F
3	Bituminous	Off	R, F
4	Bituminous	On	R, F, FA [c]

[a] R=resin, [b] F=filter, [c] FA=fly ash

2.4. Analysis of PCDD/Fs

In order to analyze the concentration of PCDD/Fs emitted whether in the gas or particle phase, the resin tubes and filters from stack sampler and fly ash sample were collected for analysis. The filters for all samples were recovered and placed in a Petri dish. The XAD–2 resin tubes were wrapped in aluminum foil. Four resin tubes, four filters and one fly ash sample were sent to Marchwood Scientific Service in United Kingdom for analysis of PCDD/Fs. The laboratory is accredited by the United Kingdom Accreditation Service (UKAS). The certificates of analysis are provided in the Supporting Material (SM).

Analysis of PCDD/Fs involved three general steps of extraction, clean–up and quantification. In extraction step, the samples were spiked with $^{13}C_{12}$ PCDD/Fs standards. Then, the spiked samples were extracted for 16 hours using Soxhlet apparatus that had been pre–cleaned with toluene. The samples were then concentrated by rotary evaporation to approximately 1 mL. Prior to clean–up process, a clean–up spike ($^{37}Cl_4$) was added to the samples. Clean–up of samples was conducted with two columns: silica gel and florisil column. The samples were applied to the silica column and eluted with hexane. The florisil column was eluted with 1% dichloromethane/hexane. Finally, the column was eluted with dichloromethane. After clean–up, the final fraction was collected, concentrated and solvent exchanged to nonane. The samples were again spiked with internal standard ($^{13}C_{12}$) prior to gas chromatography–mass spectrometry (GC–MS) analysis.

The samples were separated by GC and identified by MS (Micromass Ultima NT). The MS was calibrated using a series of five calibration standards obtained from Cambridge Isotope Laboratories. A column performance mix was also run to ensure the separation of the 2,3,7,8–TCDD isomer from near eluting TCDD isomers. The samples were auto injected onto DB–5 capillary column (60 m x 0.32 mm i.d, 0.25 μm film thickness) with helium as carrier gas in the splitless injection mode (1–2 μL). The detailed quantitative determination of PCDD/Fs was performed according to the U.S. EPA Method 1613 (U.S. EPA, 1994).

2.5. Quality Assurance (QA) / Quality Control (QC)

The criteria for ensuring the quality of dioxin analysis include the application of some QA/QC quality measures, such as continuous monitoring of laboratory contamination based on the determination of a blank samples covering the whole analytical procedure including extraction, clean–up and quantification.

3. Results and Discussion

3.1. Characteristics of PCDD/Fs emissions from the studied coal–fired power plant

The laboratory analysis of PCDD/Fs in respective media (i.e. filter, resin and fly ash) is shown in Table 5. For flue gas measurement, the reported data of Samples 1 and 2 is the total PCDD/Fs measured in filter and resin, whereas for Samples 3 and 4, the PCDD/Fs measured in filter and resin are separately reported. The amount of PCDD/Fs in particle and gas phase and the

concentrations of PCDD/Fs in flue gas are shown in Table 6. The PCDD/Fs emissions in the range of 0.0105 to 0.0137 ng I–TEQ/m³ were lower than the stipulated limit of 0.1 ng I–TEQ/Nm³ at 6% O_2 in the proposed New Environmental Quality (Clean Air) Regulation 201X (Draft). Literature data of emissions of PCDD/Fs from coal–fired power plants in other countries are summarized in Table 7. Data from oil–shale fired power plants (Schleicher et al., 2005) are also included as it is accepted that PCDD/Fs emissions from oil–shale combustion is similar as those for coal combustion (Kakareka and Kukharchyk, 2002). The reported data from the available literatures were found to be consistent with the emission rates obtained from the studied coal–fired power plant in Malaysia as presented in this paper. However, the total amount of PCDD/Fs emissions were much higher than those reported in Netherlands (Meij and Winkel, 2007), Spain (Fernandez–Martinez et al., 2004) and Poland (for Poland, such result applies on pulverized coal technology only) (Grochowalski and Konieczynski, 2008). This is further explained by congener distribution as discussed below.

The results showed that the formation of PCDDs was less than PCDFs, similarly as reported by Lin et al. (2007) and Grochowalski and Konieczynski (2008). Vogg et al. (1987) studied PCDD/Fs content in fly ash at various temperatures between 200 to 400 °C and found that the content of PCDDs was consistently lower than that of PCDFs. In addition, DOE (1989) also reported lower PCDDs than PCDFs for several emission sources such as municipal incinerators, coal–fired power plants and industrial coal burning. U.S. EPA (2006) reported that decrease in oxygen content during combustion generally increases the PCDDs yield. This could probably be the reason for lower PCDD amounts since coal combustion occurs at the optimum oxygen level. Junk and Richard (1981) reported that tetrachloro dibenzo–p–dioxin (TCDD) was not detected in the power plant burning coal supplemented with processes municipal waste due to high combustion temperature of ~1 200 °C, adequate oxygen supply with excess air ~22% and long residence time >1.3s.

The PCDD/Fs congener distribution in flue gas and fly ash are shown in Figures 2 to 8. Referring to Figures 2 and 3 which represent PCDD/Fs emission during normal plant operation, the dominant congener is 2,3,7,8–TCDF followed by 1,2,3,7,8–PCDF and 2,3,4,7,8–PCDF. This is different from the results reported by Fernandez–Martinez et al. (2004) and Lin et al. (2007) which demonstrated OCDD as the dominant congener followed by OCDF. It is worth to note that increasing chlorine substitution (from four to eight chlorine atoms) generally results in a marked decrease in toxicity. As described in Section 1, TEF for TCDF is 0.1, hundredfold higher than OCDD and OCDF of 0.001. Therefore, this results in higher PCDD/Fs emissions in the studied plant than those reported in literature (see Table 7).

For fly ash (see Figure 4), it can be observed that as the chlorinated level increases, the concentration of PCDD/Fs roughly shows an increasing pattern (note that some congeners however show slight reduction). Due to the lack of literature data on fly ash from coal–fired power plants, comparison was made with muni-cipal solid waste incinerator (MSWI). The congener distribution was found similar with the pattern reported by Zhang et al. (2012) and Chang and Huang (1999). Chang and Huang (1999) reported that lower chlorinated congeners have favorable desorbing reactions and therefore may escape from fly ash more readily than higher–chlorinated ones, leaving the latter in fly ash.

PCDFs/PCDDs ratio is used to suggest formation mechanism, source identification and atmospheric transport (Buekens et al., 2000; Zhang et al., 2012). PCDFs/PCDDs ratio obtained in this study ranges from 1.0 to 7.2 (Table 5). A review by Huang and Buekens (1995) indicates that PCDFs/PCDDs ratio for *de novo* synthesis was generally more than 1, whereas for precursor formation the ratio was less than 1. Therefore, it is suggested that the formation of

PCDD/Fs in the studied coal–fired power plant could be via *de novo* synthesis. This could be supported with the presence of PCDD/Fs in fly ash of 0.0075 ng/g. Zhang et al. (2012) also proposed that *de novo* synthesis was dominant in their study based on PCDFs/PCDDs ratio of 1.82 and 1.94 in stack gas and fly ash, respectively. Likewise, Littarru (2006) reported the occurrence of *de novo* synthesis mechanism based on PCDFs/PCDDs ratio of more than 1 and typical isomeric composition.

3.2. Partitioning of PCDD/Fs emissions in particle and gas phase

The knowledge on partitioning of PCDD/Fs compounds is important in the selection of control devices and to determine the pollutants transport and deposition. The results of this study showed that 95% of PCDD/Fs was collected in resin and only 5% was collected in filter media as shown in Table 6, indicating that the emission of PCDD/Fs from the stack was mainly in the gas phase. Previous studies also showed similar results (Cavallaro et al., 1982; Ballschmiter et al., 1984; Benfenati et al., 1986; Chi et al., 2006). Among the factors affecting the partitioning of PCDD/Fs in gas/particle phase was temperature as reported by Chi et al. (2006). Further investigations are required to elucidate such effects in this study.

Figures 5 to 8 show the distribution of PCDD/Fs congeners in particulate and gas phases. For Sample 3, higher chlorinated congeners were observed in particulate phase (Figure 5) and lower chlorinated congeners in gas phase (Figure 6). This is expected as the vapor pressure decreases with increasing chlorination causing lower chlorinated congeners to become more volatile compared to higher chlorinated congeners. Sample 4 (F) (Figure 7) demonstrates similar trend with Sample 3 (F) (Figure 5). However, Sample 4 (R) (Figure 8) exhibits different distribution pattern for PCDD with high concentrations of higher chlorinated congener in gas phase.

Table 5. *Laboratory analysis of PCDD/Fs in sampling media*

Sample ID	1 (R [a]+F [b])	2 (R+F)	3 (F)	3 (R)	4 (F)	4 (R)	4 (FA [c])
Sampled gas flow rate (Nm^3)	4.81	4.727	4.661	4.661	4.675	4.675	N.A [d]
Oxygen level (%)	6.1	5.3	6.1	6.1	5.9	5.9	N.A [d]
Particles (mg)	23.28	18.48	72.75	72.75	41.39	41.39	N.A [d]
Congener (ng)							
Dioxins							
2,3,7,8-TCDD	0.0168	0.0108	(0.0006) [e]	0.0113	(0.0008) [e]	0.0071	(0.0013) [e]
1,2,3,7,8-PCDD	0.0066	0.0029	(0.0004) [e]	0.0063	(0.0006) [e]	0.0086	(0.0011) [e]
1,2,3,4,7,8-HxCDD	0.0014	0.0014	(0.0005) [e]	0.0011	(0.0007) [e]	0.0049	0.003
1,2,3,6,7,8-HxCDD	0.002	0.0021	0.0007	0.0017	(0.0007) [e]	0.015	0.005
1,2,3,7,8,9-HxCDD	0.0011	0.0012	(0.0004) [e]	0.0008	(0.0006) [e]	0.0057	0.0033
1,2,3,4,6,7,8-HpCDD	0.009	0.007	0.0037	0.0044	0.0043	0.0527	0.0168
OCDD	0.0258	0.0147	0.0089	0.0122	0.011	0.0878	0.0343
Furans							
2,3,7,8-TCDF	0.1941	0.1353	0.001	0.1354	(0.0006) [e]	0.0519	(0.0009) [e]
1,2,3,7,8-PCDF	0.0495	0.0412	0.0012	0.0503	(0.0004) [e]	0.0417	0.0032
2,3,4,7,8-PCDF	0.0404	0.037	0.0014	0.0424	0.0017	0.0336	0.003
1,2,3,4,7,8-HxCDF	0.0116	0.0162	0.002	0.0115	0.0025	0.0176	0.0058
1,2,3,6,7,8-HxCDF	0.0102	0.0147	0.0014	0.0103	0.001	0.0198	0.0052
2,3,4,6,7,8-HxCDF	0.0064	0.0121	0.0005	0.0065	0.0013	0.0186	0.0065
1,2,3,7,8,9-HxCDF	0.0005	0.0041	0.0003	(0.0004) [e]	(0.0005) [e]	0.0078	0.0061
1,2,3,4,6,7,8-HpCDF	0.0116	0.0168	0.005	0.0103	0.0052	0.0351	0.014
1,2,3,4,7,8,9-HpCDF	0.0015	0.0028	0.0006	0.0012	0.0009	0.0097	0.0064
OCDF	0.0073	0.0049	0.0026	0.0042	0.0034	0.035	0.0168
Total PCDDs	0.0627	0.0401	0.0133	0.0378	0.0153	0.1818	0.0624
Total PCDFs	0.3331	0.2851	0.016	0.2721	0.016	0.2708	0.067
PCDFs/PCDDs ratio	5.3	7.1	1.2	7.2	1.0	1.5	1.1
Total PCDD/Fs	0.3958	0.3252	0.0293	0.3099	0.0313	0.4526	0.1294
Total PCDDs (I-TEQ)	0.0451	0.039	0.0014	0.0402	0.0017	0.0311	0.0044
Total PCDFs (I-TEQ)	0.0206	0.0128	0.001	0.0149	0.0014	0.0148	0.0031
Total I-TEQ (ng)	0.0657	0.0518	0.0024	0.0551	0.0031	0.0459	0.0075

[a] R=resin, [b] F=filter, [c] FA=fly ash
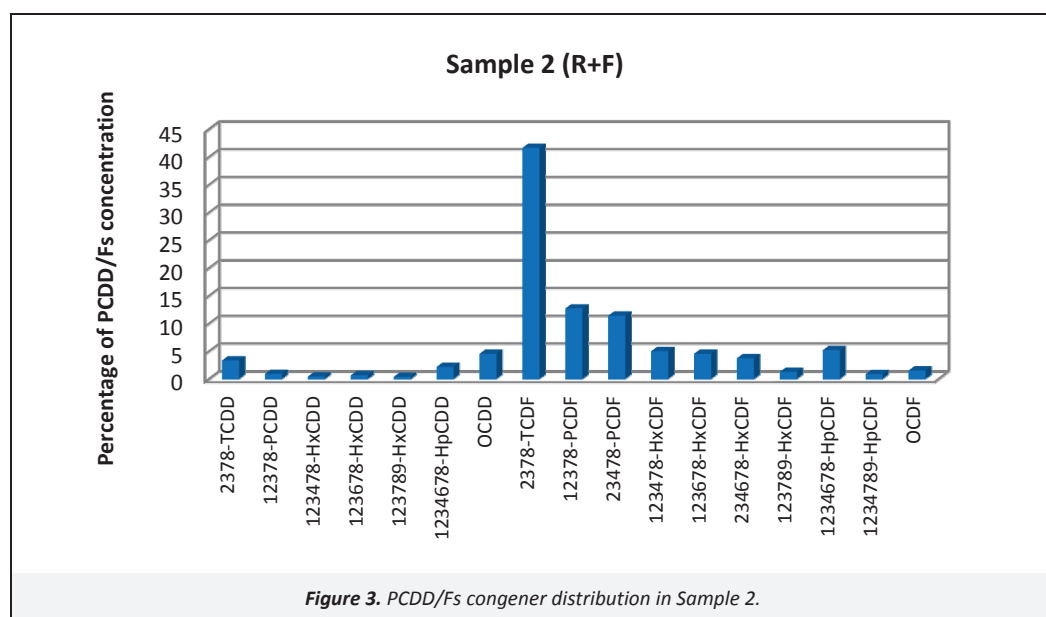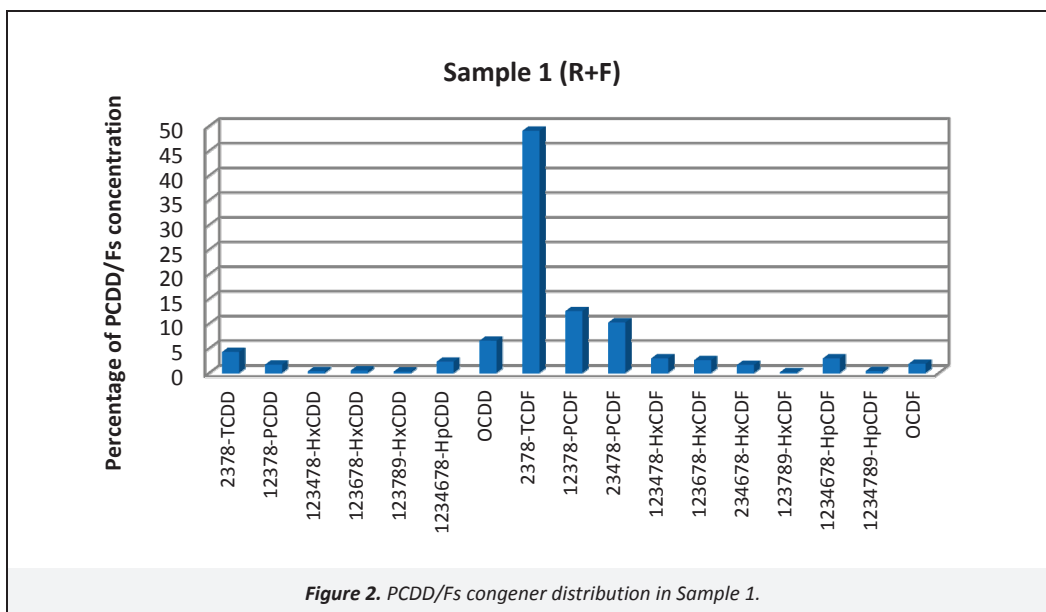[d] N.A: not applicable
[e] Not detected or quantified. Detection limits are presented in brackets.
T=tetra, Hx=hexa, Hp=hepta, O=octa, TEQ=toxic equivalent
TEFs (NATO) were used to determine TEQs

Table 6. *Concentrations of PCDD/Fs in flue gas at 6% O_2 and the established emission factors for the studied coal-fired power plant*

	Run ID			
	1	2	3	4
Sampled gas flow rate (dry, Nm^3)	4.81	4.727	4.661	4.675
PCDD/F in particle phase (ng)	NT [a]	NT [a]	0.0024	0.0031
PCDD/F in gas phase (ng)	NT [a]	NT [a]	0.0551	0.0459
Total PCDD/F collected (ng I-TEQ)	0.0657	0.0518	0.0575	0.049
PCDD/F concentration (ng I-TEQ/Nm^3)	0.0137	0.011	0.0123	0.0105
% PCDD/F in particle phase	NT [a]	NT [a]	4.01	5.99
% PCDD/F in gas phase	NT [a]	NT [a]	95.99	94.01
Emission factor (ng I-TEQ/kg coal feed)	0.11	0.08	0.09	0.08

[a] *NT: Not tested*

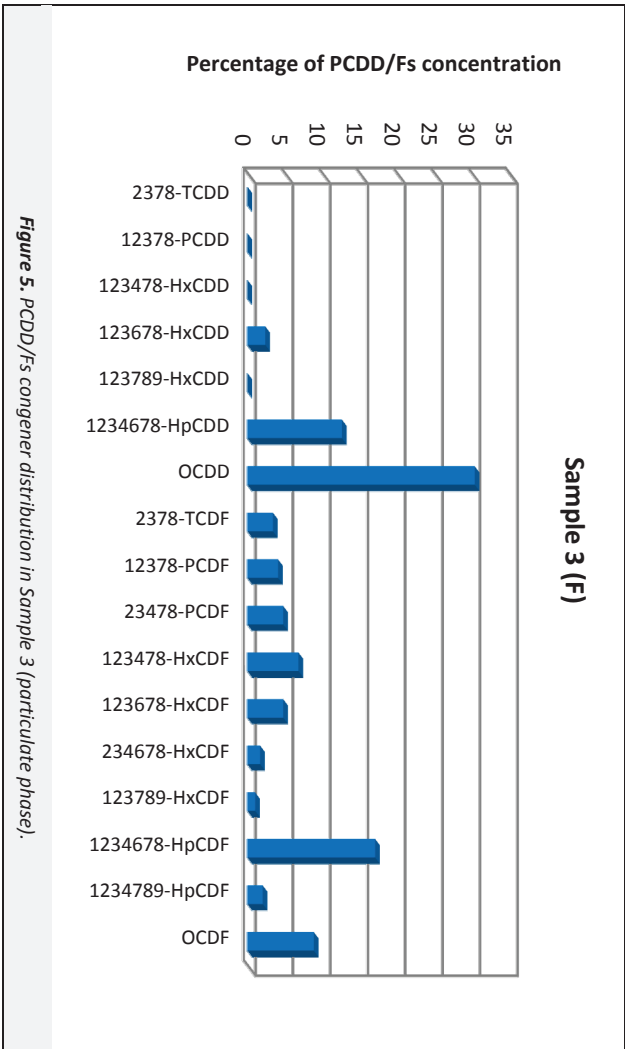

Figure 2. *PCDD/Fs congener distribution in Sample 1.*

Figure 3. *PCDD/Fs congener distribution in Sample 2.*

Percentage of PCDD/Fs concentration
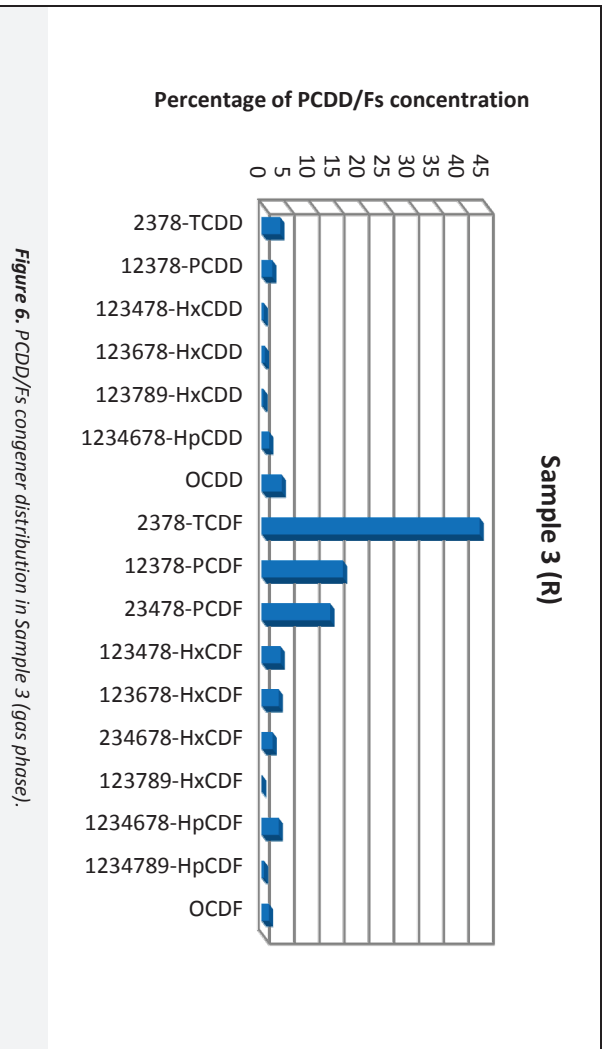
Sample 3 (R)

Figure 6. PCDD/Fs congener distribution in Sample 3 (gas phase).

Percentage of PCDD/Fs concentration

Sample 3 (F)

Figure 5. PCDD/Fs congener distribution in Sample 3 (particulate phase).
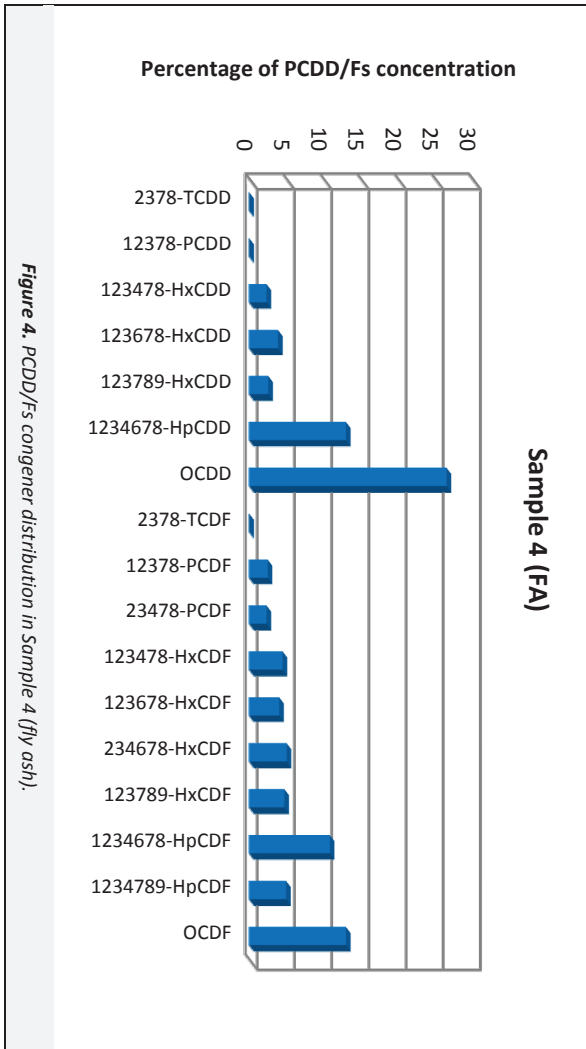
Percentage of PCDD/Fs concentration

Sample 4 (FA)

Figure 4. PCDD/Fs congener distribution in Sample 4 (fly ash).

High removal of particles by ESP might be the reason for low PCDD/Fs emission in particle phase (Guerriero et al., 2009). Sampling of TCDD at different points of an incinerator by Benfenati et al. (1986) showed that removal of TCDD in particle phase by ESP has resulted in high amount of TCDD emitted from the stack in gas phase. Removal of PCDD/Fs in particle phase by ESP was proven in this study with the presence of PCDD/Fs (0.0075 ng/g) in fly ash. Due to the very low PCDD/Fs emissions in particle phase measured at the stack, it could be speculated that ESP in the studied coal–fired power plant with removal efficiency of 99% had effectively removed particle phase PCDD/Fs.

3.3. Effect of coal quality and air pollution control device (APCD) configuration on PCDD/Fs emissions

The results in Table 6 demonstrate that type of coal influenced the formation of PCDD/Fs during combustion. Bituminous coal with high S content results in slightly lower PCDD/Fs emissions compared to sub–bituminous coal. Sulfur has been numerously reported for its capability to inhibit PCDD/Fs formation in MSW incinerator (Thomas and McCreight, 2008; Aurell et al., 2009; Wu et al., 2012) and there were studies suggested that co–firing MSW with coal could reduce PCDD/Fs emissions (Yan et al., 2006; Gulyurtlu et al., 2007). This could be achieved since S content in coal can reach up to 10% w/w while S content in MSW is normally less than 1% w/w.

Sulfur inhibits formation of PCDD/Fs mainly in two ways; by converting chlorine molecule into hydrogen chloride (HCl), and hindering the copper–catalyst surface already existing on fly ash particles. The mechanisms of PCDD/Fs inhibition by sulfur are described by the following equation (Thomas and McCreight, 2008).

$$Cl_2 + SO_2 + H_2O = 2HCl + SO_3 \tag{1}$$

$$CuO + SO_2 + 1/2O_2 = CuSO_4 \tag{2}$$

In addition, the results in Table 6 show that when FGD was in operation, the emission of PCDD/Fs was lower than that when FGD was off. Similar finding was reported by Meij and Winkel (2007) in a plant equipped with FGD. This indicated that there were some removal effects of PCDD/Fs by FGD. It was observed that the temperature of flue gas measured in this study was 150 °C when FGD off and the operation of FGD had reduced the temperature of flue gas down to 100 °C.

Comparison of Figures 1 and 2 shows that FGD does not influence the pattern of congener distribution. Similar observation was reported by Hutson et al. (2009) in their study on the effect to PCDD/Fs emissions due to brominated PAC (Poly activated carbon) injection for mercury removal. They observed no influence on the PCDD/Fs distribution pattern with or without the injection. This may suggest that pollution control system would reduce the emission concentration but not changing the congener distribution.

3.4. Establishment of emission factors of PCDD/Fs in the studied coal–fired power plant

The emission factors for PCDD/Fs from the studied coal–fired power plant were determined using the following equation, modified from U.S. EPA (1997):

$$Emission\ Factor=$$
$$\frac{Pollutant\ concentration\ \left(\frac{ng}{Nm^3}\right)\ x\ Flue\ gas\ flow\ rate\ (\frac{Nm^3}{h})}{Coal\ feeding\ rate\ \left(\frac{kg}{h}\right)} \tag{3}$$

Table 6 lists the established emission factors for each combustion condition. The emission factors range from 0.08 to 0.11 ng I–TEQ/kg, which is higher than oil–shale fired power plant (Table 7). Nevertheless, Kakareka and Kukharchyk (2002) reported an emission factor of 0.02 ng I–TEQ/kg for both coal and oil–shale fired power plants in European Countries.

Emission factors during operation of ESP without FGD (0.11 and 0.09 ng I–TEQ/kg coal feed) were found to be slightly higher to that reported by the U.S. EPA (2006) of 0.079 ng I–TEQ/kg for coal–fired power plant equipped with ESP only, but much higher when compared with emission factors obtained in Spain (Table 7) for the same APCD configuration. For emission factors obtained during operation of both ESP and FGD (0.08 ng I–TEQ/kg), the value was lower than Taiwan (Table 7). This implied that APCD configuration of ESP and FGD in the studied coal–fired power plant was efficient in removing PCDD/Fs. Highest emission factors were observed for coal combustion using coal–fired circulating fluidized bed technology in Poland (Table 7), indicating that the inconsistency in emission factors was mostly due to divergence in types of coal, combustion technology, and APCD configuration in coal–fired power plants.
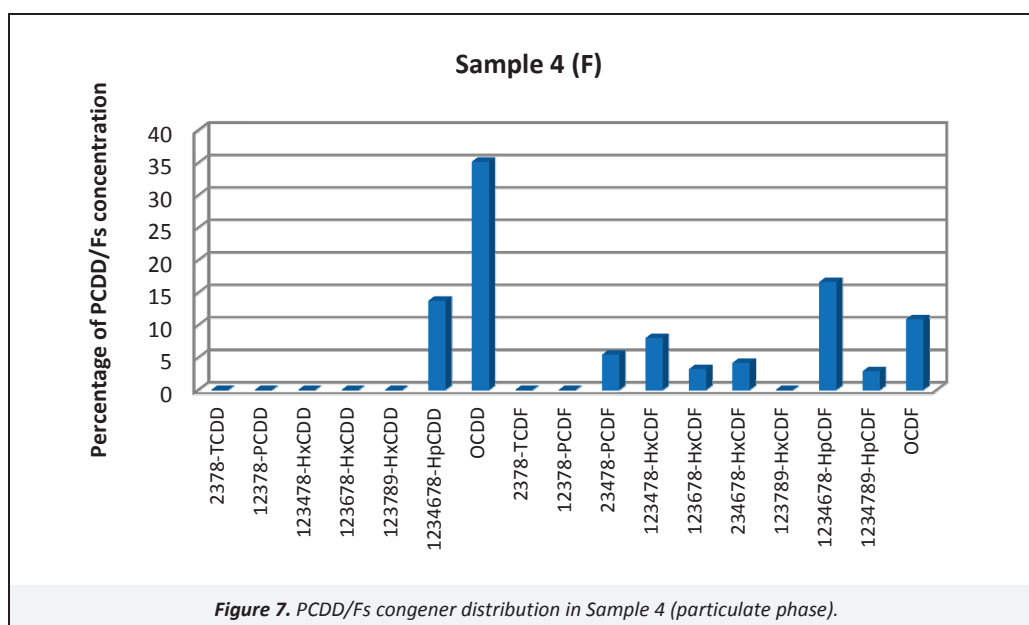

***Figure 7.** PCDD/Fs congener distribution in Sample 4 (particulate phase).*
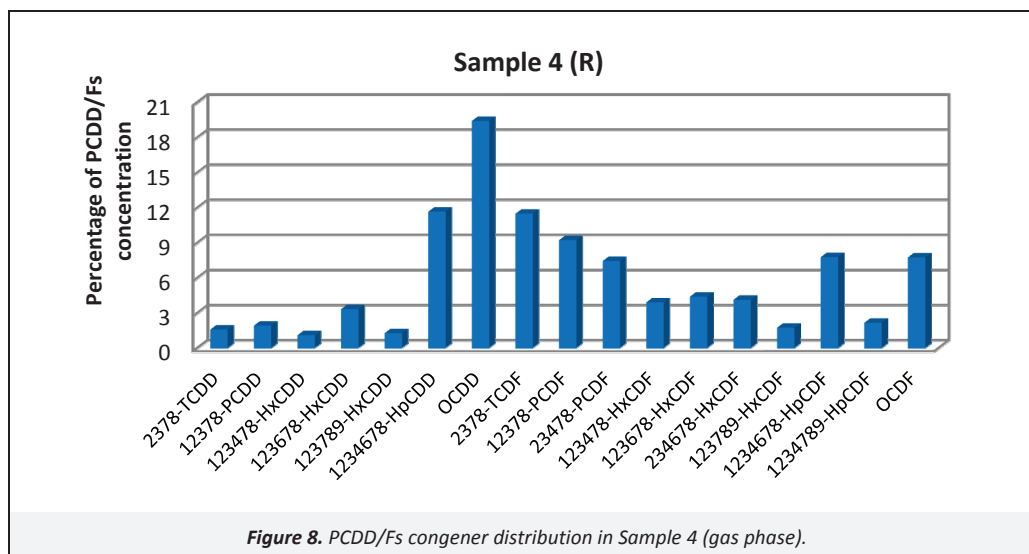
Figure 8. *PCDD/Fs congener distribution in Sample 4 (gas phase).*

Table 7. *PCDD/Fs emissions from power plants in other countries*

Country	Fuel/Combustion Technology/APCD Configuration	PCDD/Fs (ng I–TEQ /Nm^3)	Emission Factors (ng I–TEQ/kg)	References
Estonia	Balti Power Plant Fuel: oil–shale	0.0029–0.0039 (at 10% O$_2$) 0.004–0.0053 (at 6% O$_2$)	0.017–0.024	Schleicher et al. (2005)
	Eesti Power Plant Fuel: oil–shale	0.0008–0.0015 (at 10% O$_2$) 0.0011–0.002 (at 6% O$_2$)	0.0023–0.0043	
Taiwan	Coal–fired power plant ML: SCR+ESP+FGD	0.002–0.031	0.133	Lin et al. (2007)
	Coal–fired power plant TC: SCR+ESP+FGD	0.068–0.345	1.11	
Netherlands	ESP+FGD	0.0015–0.0032	NA [a]	Meij and Winkel (2007)
Spain	Data from 4 conventional coal–fired technology with ESP and 1 pressurized fluidized bed power plant	5x10^{-5}–0.009	2.8x10^{-4}–0.005	Fernandez–Martinez et al. (2004)
Poland	Pulverized coal	0.0012–0.0032	NA [a]	Grochowalski and Konieczynski (2008)
	Coal–fired circulating fluidized bed (CFB)	0.012–0.060 (at 6% O$_2$)	7.51–46.4	

[a] NA: not available

4. Conclusion

PCDD/Fs have been known to pose health effects and coal–fired power plants are among the anthropogenic sources of PCDD/Fs. Malaysia has quite a number of coal–fired power plants, but there has not been any study reporting the emissions level especially for PCDD/Fs. Thus, in this study the measurement of PCDD/Fs emissions from a coal–fired power plant in Malaysia was presented which discussed (1) partitioning of PCDD/F in particle and gas phase (2) effects of coal quality to PCDD/Fs formation, (3) effects of air pollution control device (APCD) configuration to PCDD/Fs formation, and (4) establishment of emission factors for PCDD/Fs from the studied coal–fired power plant.

The measured PCDD/Fs emissions in the range of 0.0105 to 0.0137 ng I–TEQ/m^3 were much lower than the Malaysian stipulated limit of 0.1 ng I–TEQ/Nm^3 at 6% O$_2$ in the proposed new Environmental Quality (Clean Air) Regulation 201X (Draft). The results on measurement of PCDD/Fs emissions presented in this study were mostly in good agreement with the previous works conducted in other countries on PCDD/Fs emissions. Laboratory analysis of sampling media (i.e. filter, resin and fly ash) showed that PCDFs were the dominant congeners. The emissions of PCDD/Fs were low most probably due to the high combustion efficiency. The PCDFs/PCDDs ratio was more than 1 and PCDD/Fs were detected in fly ash, hence suggesting that the formation of PCDD/Fs during coal combustion was mainly through *de novo*

synthesis. Analysis on PCDD/Fs content in filter and XAD–2 resin media showed that PCDD/Fs were mainly emitted in gas phase. Measurement of emissions during combustion of bituminous and sub–bituminous coal indicated that formation of PCDD/Fs was influenced by type of coal. Combustion of bituminous coal with high S content resulted in lower PCDD/Fs emissions. It was also found that operation of flue gas desulfurization (FGD) reduced the emissions of PCDD/Fs.

The established emission factors were in the range of 0.08 to 0.11 ng I–TEQ/kg coal feed. The established emission factors are useful for pre–development assessment of new coal–fired power plant in Malaysia by making the assessment much easier, faster and most importantly, more reliable. Besides, the results could assist the Department of Environment Malaysia in finalizing the proposed new Environmental Quality (Clean Air) Regulation 201X (Draft) and could provide an important database to assist the decision makers for formulating policies to control the impact of PCDD/Fs emissions from coal–fired power plants.

Supporting Material Available

Certificate of PCDD/Fs analysis. This information is available free of charge via the Internet at http://www.atmospolres.com.

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